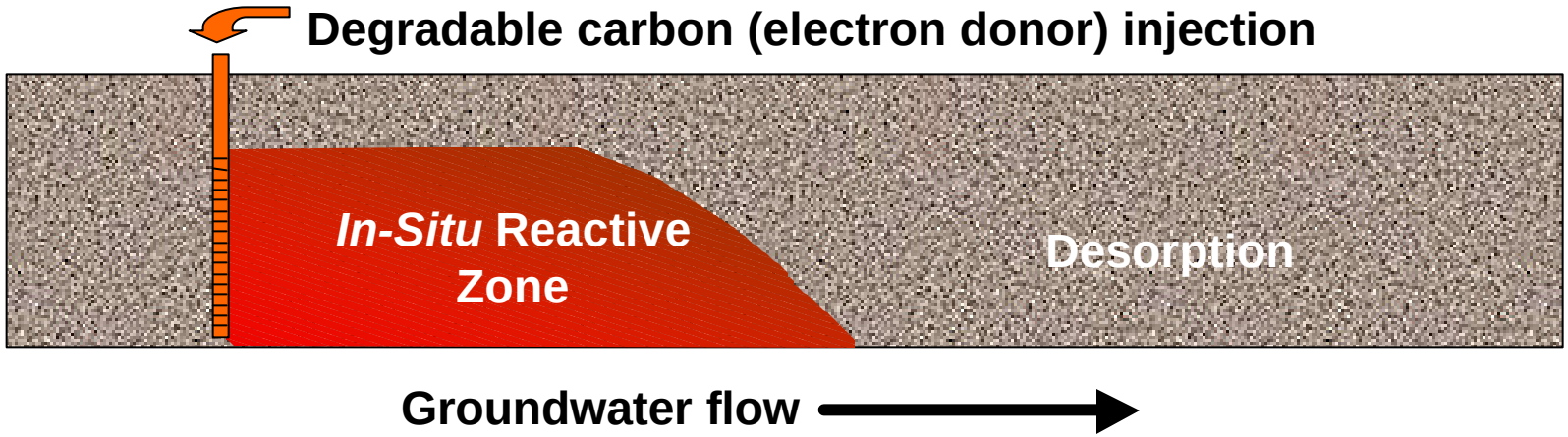
Engineered Anaerobic Systems Via *In-Situ* Reactive Zones



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April 2003

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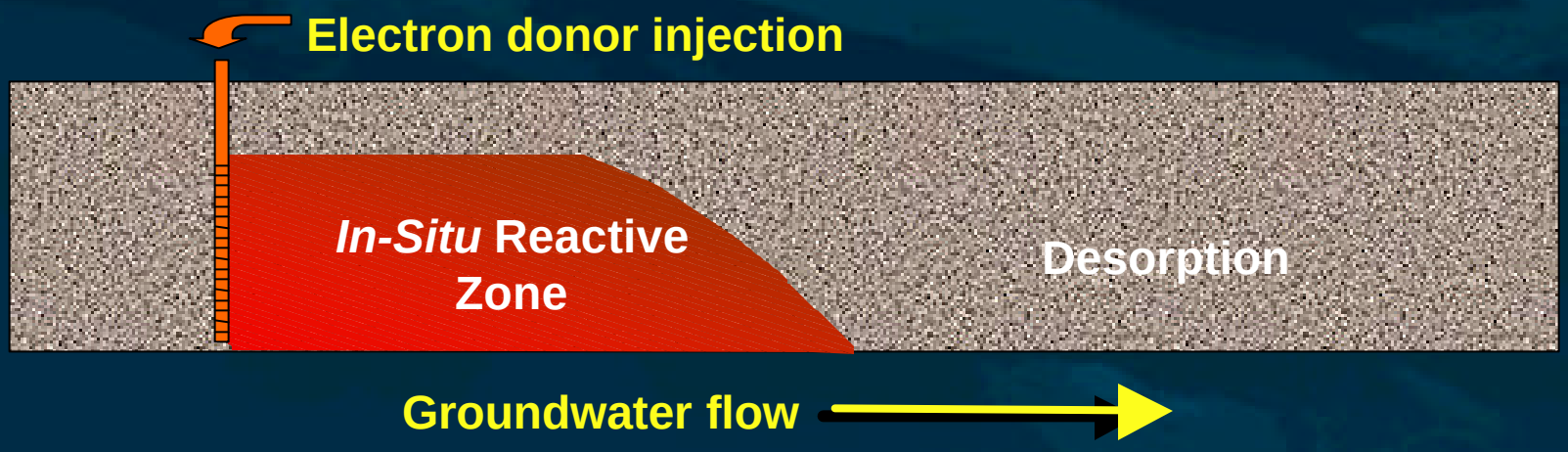
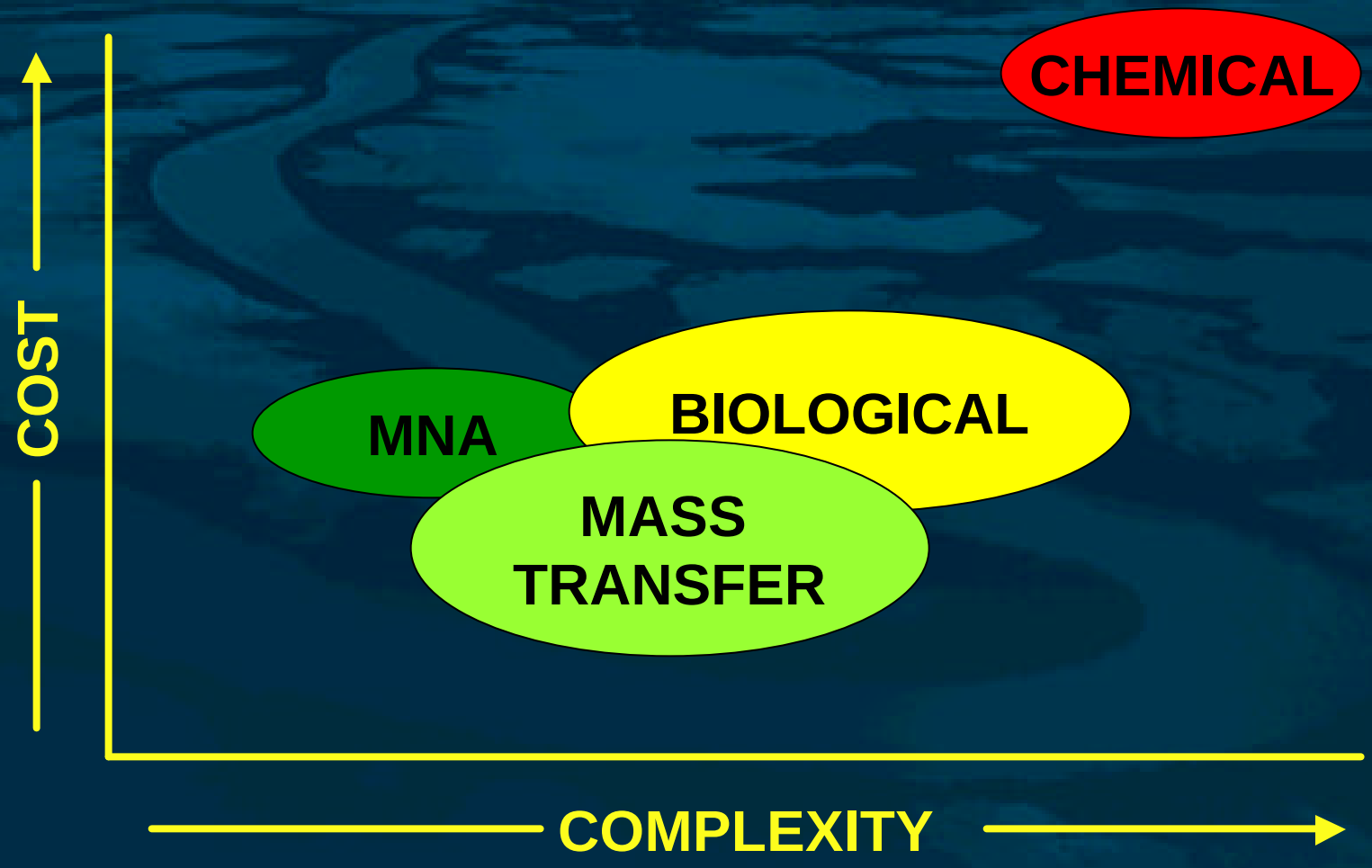
Questions to be answered:

- What is an *in-situ* reactive zone (IRZ)?
- Why would you use an IRZ?
- What's the benefit of an IRZ?
- How do you develop an IRZ?

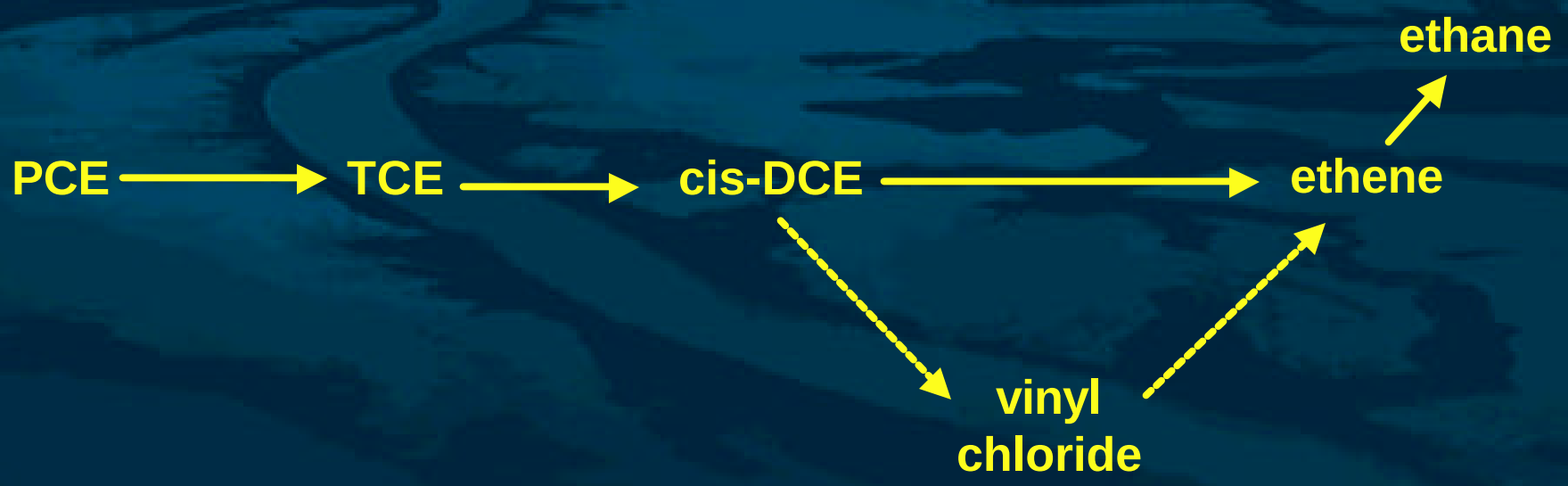


Why Use an IRZ?



Carbon Oxidation State And Remedy Selection

Reductive Dechlorination Strategy

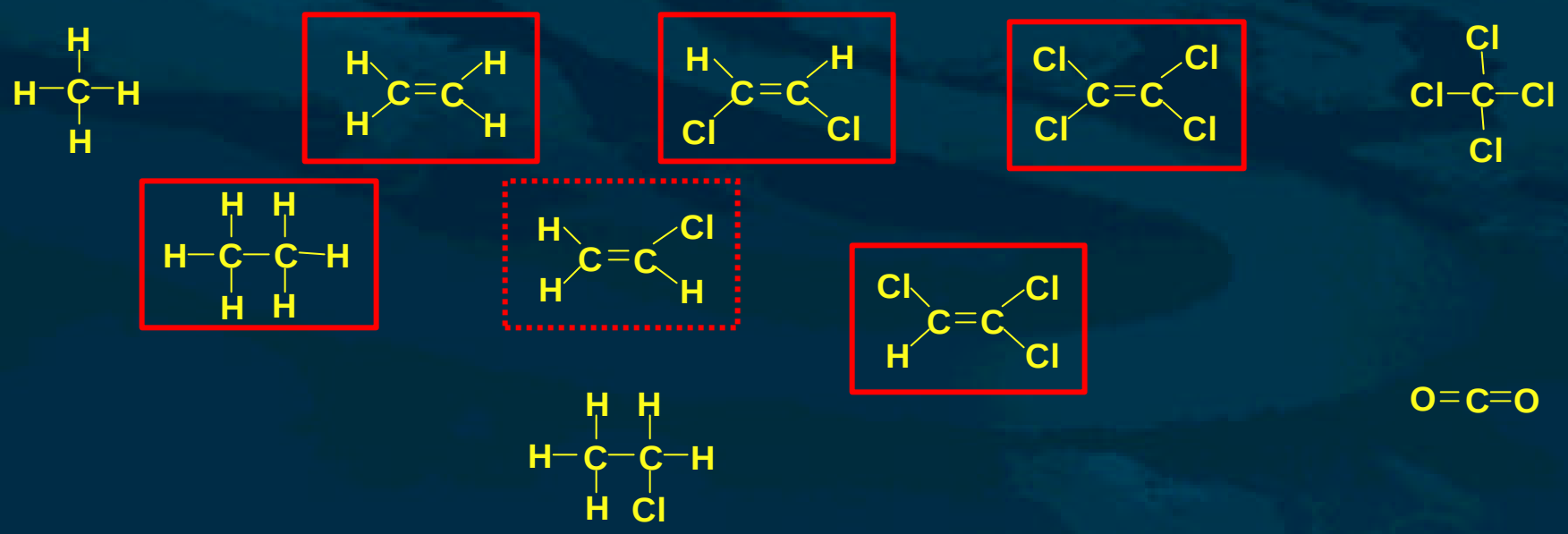


Selecting a Remedial Technology

Oxidation States of Common Contaminant Molecules

REDUCED — **OXIDIZED**

- 4 | - 3 | - 2 | - 1 | 0 | 1 | 2 | 3 | 4



Microbial Ecology

- Microorganisms need to eat and "breathe"
- Food source – electron donor (e.g., natural organic matter or suitable contaminant)
- Respiration source – electron acceptor (e.g., DO, nitrate, ferric iron, sulfate, carbon dioxide, suitable contaminant)
- During metabolism:
  - The electron donor (food source) is oxidized
  - The electron acceptor is reduced

Basic Aquifer Metabolism

Electron Donor = food glucose glucose

+

Electron Acceptor = breathing air oxygen nitrate

Aquifer Microbial Community

carbon dioxide carbon dioxide **Oxidized Electron Donor**

+

nitrite water **Reduced Electron Acceptor**

+

460 kcal/mol 676 kcal/mol **Energy**

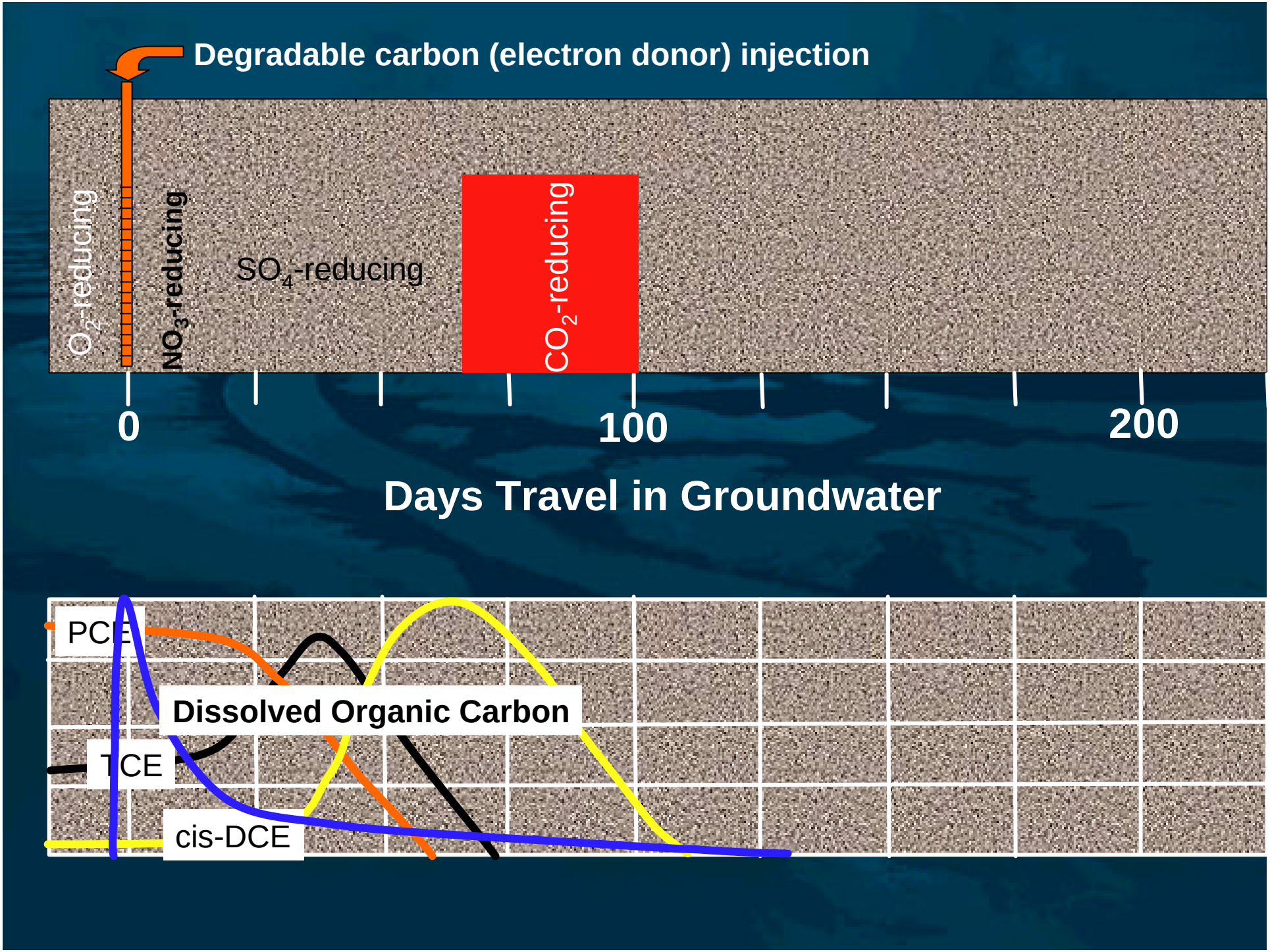
Energy Yield of Metabolic Alternatives

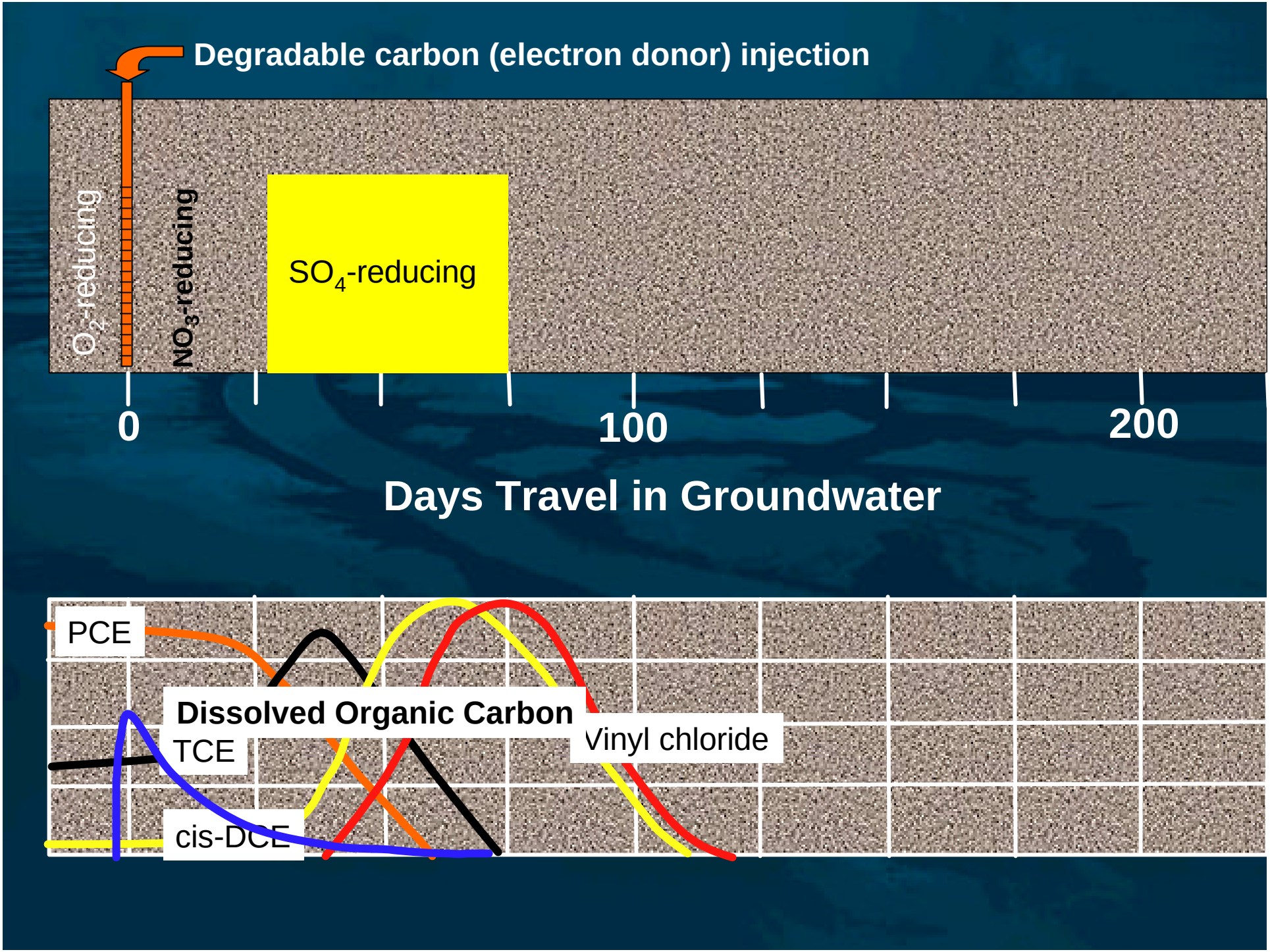
	Electron acceptor	Reduced Product	Energy Yield [a] ?G (kcal/mol)
	Oxygen (O_2)	H_2O	- 676
	Nitrate (NO_3)	Nitrite (NO_2)	- 460
	Nitrite (NO_2)	Nitrogen (N_2)	- 720
PCE TCE	Sulfate (SO_4^{2-})	Sulfur (S)	- 132
Cis-DCE VC	Carbon Dioxide (CO_2)	Methane (CH_4)	- 96

[a] For the complete oxidation of glucose ($C_6H_{12}O_6$) to carbon dioxide (CO_2)

Microbial Ecology of Reductive Dechlorination

- Species that gain the most energy from metabolic conversion of carbon sources are the most competitive;
- Therefore, as long as oxygen is present, oxygen-using species dominate the system (other species are present, but lie in the background);
- When the rate of carbon supply exceeds the rate of oxygen supply, oxygen will be completely consumed and further metabolism is achieved through the consumption of other electron acceptors (e.g. nitrate first, then ferric iron).
- When the aquifer microbial community reaches CO_2 reduction, high-performance reductive dechlorination can occur.


Degradable carbon (electron donor) injection
O_2-reducing
NO_3-reducing
SO_4-reducing
CO_2-reducing
0
100
200
Days Travel in Groundwater
PCE
Dissolved Organic Carbon
TCE
cis-DCE


Degradable carbon (electron donor) injection
O_2-reducing
NO_3-reducing
SO_4-reducing
0
100
200
Days Travel in Groundwater
PCE
Dissolved Organic Carbon
TCE
Vinyl chloride
cis-DCE

Basic Challenges for Anaerobic IRZs

Modify the aquifer ecosystem to accomplish the following:

- **Increase electron donor supply to favor "low-redox" microbial consortia**
- **Create a chemical habitat with high electron mobility and availability of molecular hydrogen**
- **Promote contaminant desorption**
- **Achieve contaminant reduction through microbial processes and direct chemical hydrogenation reactions**

Monitor and manage the treatment process carefully:

- **Avoid excessive fermentation and the associated pH excursions**
- **Overcome electron acceptor recharge**
- **Prevent stalling of the reductive dechlorination sequence (accumulation of cis-1,2-DCE or vinyl chloride)**

Design Variables for Anaerobic IRZs

Site-Specific Constraints

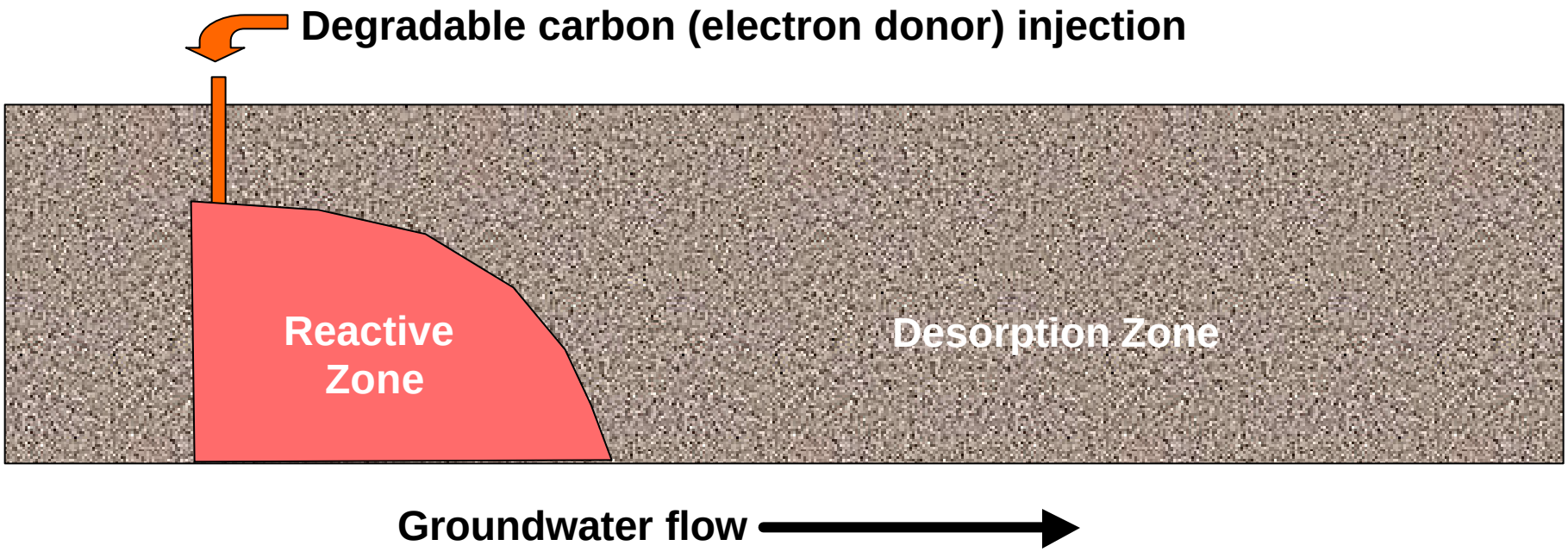
- Groundwater velocity
- Aquifer organic carbon content (f_{oc})
- Electron acceptor recharge rates
- Aquifer buffering capacity
- Background contaminant half-life in the aquifer
- Influent aqueous-phase contaminant concentrations

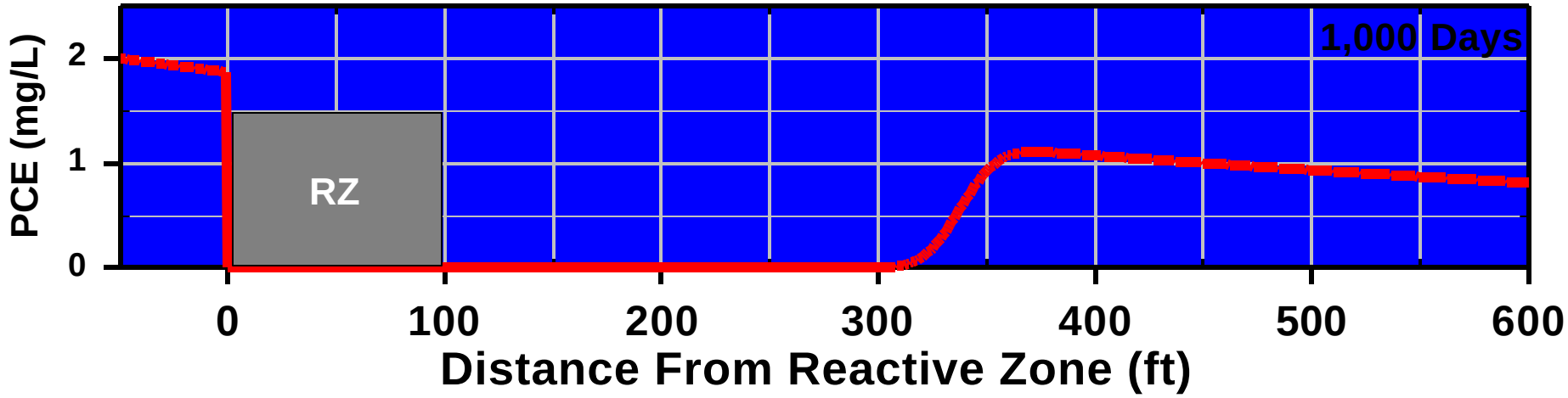
System Design Choices

- Remedial objectives
  - Concentration targets
  - Time to completion
- Carbon source degradation kinetics
- Carbon loading rate

Two Modes of Anaerobic IRZ Treatment:

- Direct destruction in the reducing zone
- Desorption in downgradient aquifer


Degradable carbon (electron donor) injection
Reactive Zone
Desorption Zone
Groundwater flow


1,000 Days
RZ
PCE (mg/L)
0
1
2
0
100
200
300
400
500
600
Distance From Reactive Zone (ft)

How to Choose an Electron Donor

- Cost per mole of reduced carbon
  - Use low-cost, food-grade materials
  - Rate of consumption in the aquifer
  - Must exceed electron acceptor recharge rates
- Mobility in the aquifer
  - Must disperse sufficiently to create a reactive zone that spans the aquifer, vertically and horizontally

Electron Donor	Bulk Price $/lb	$/lb of PCE
Food-Grade Donors		
Milk	0.05	0.18
Molasses	0.20 - 0.35	0.16
Sugar (Corn Syrup)	0.25 - 0.30	0.40
Whey	0.05	0.04
Edible Oils	0.20 - 0.50	NA
Flour (Starch)	0.30	0.85
Other Commercial Donors		
Sodium Lactate	2.20	NA
Chitin	2.25 - 3.00	NA
Methyl Cellulose	4.00 - 5.00	NA
HRC$_{TM}$	12.00	NA

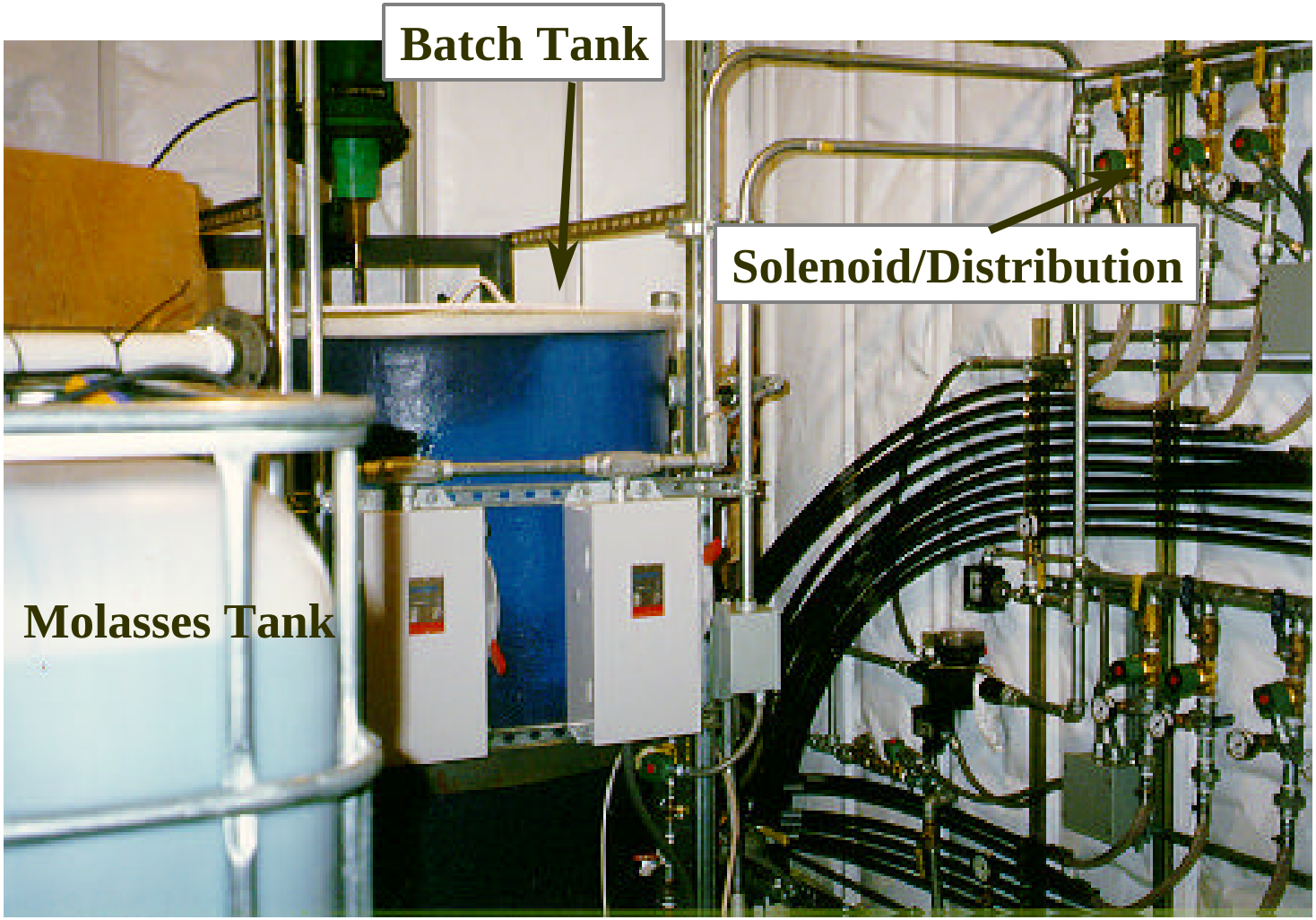
NA — Not Analyzed.

Source: Harkness, et.al., 2000.

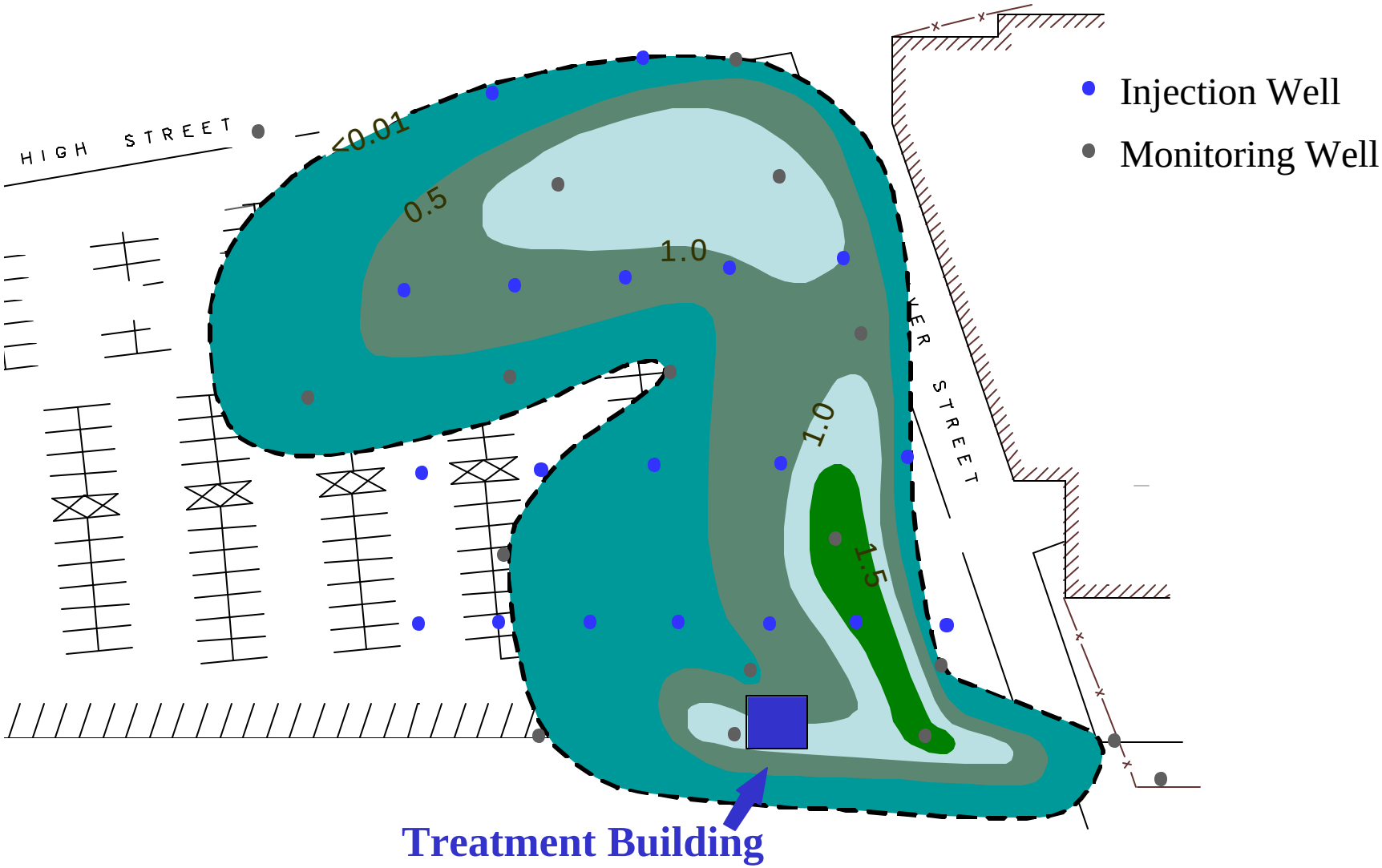
A variety of food-grade substances have been used in laboratory and field studies. This table summarizes some of those reported in the literature.

Hexavalent Chromium Site

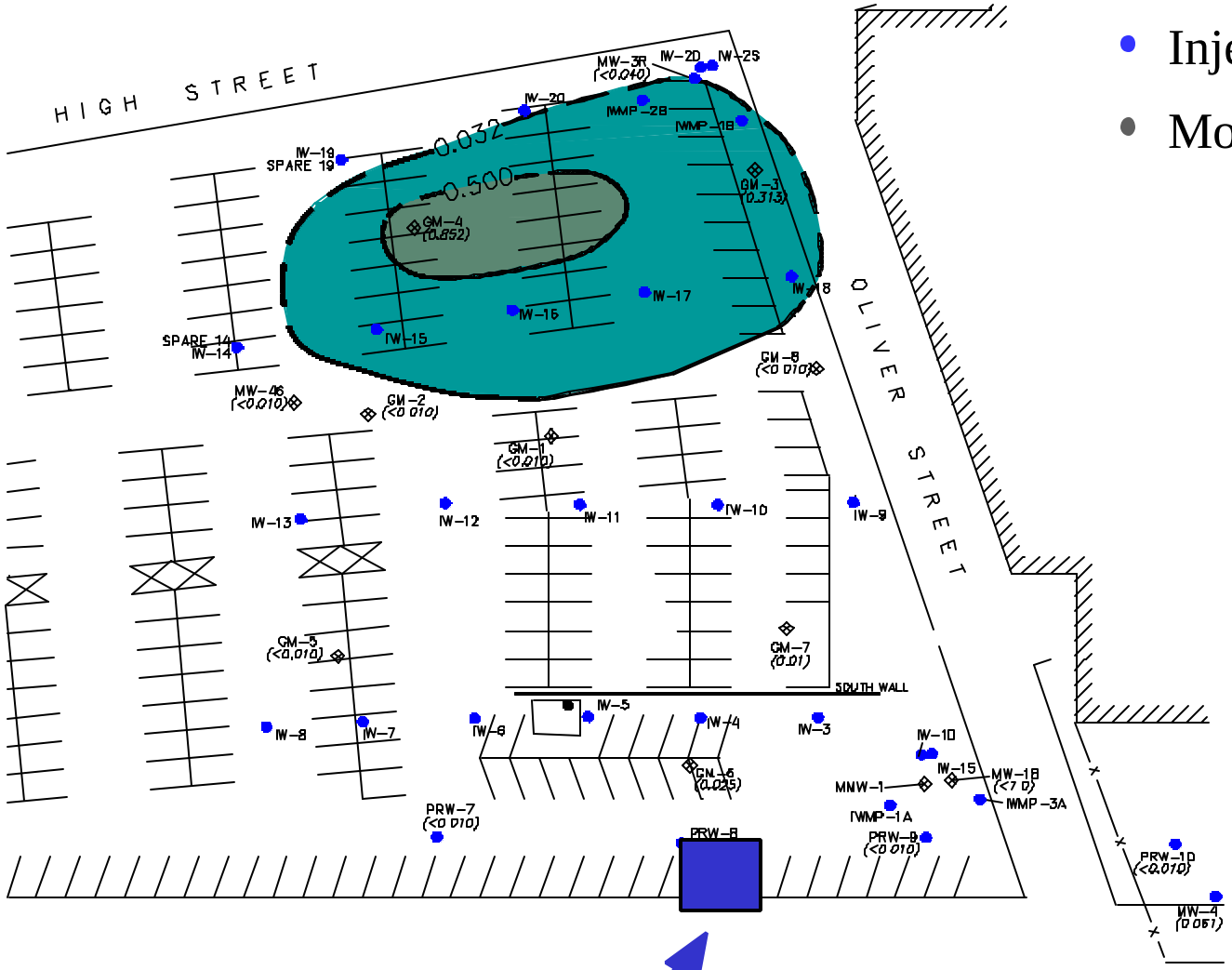
Molasses Injection System



Cr^{6+} Plume January 1997



Cr^{6+} Plume July 1998

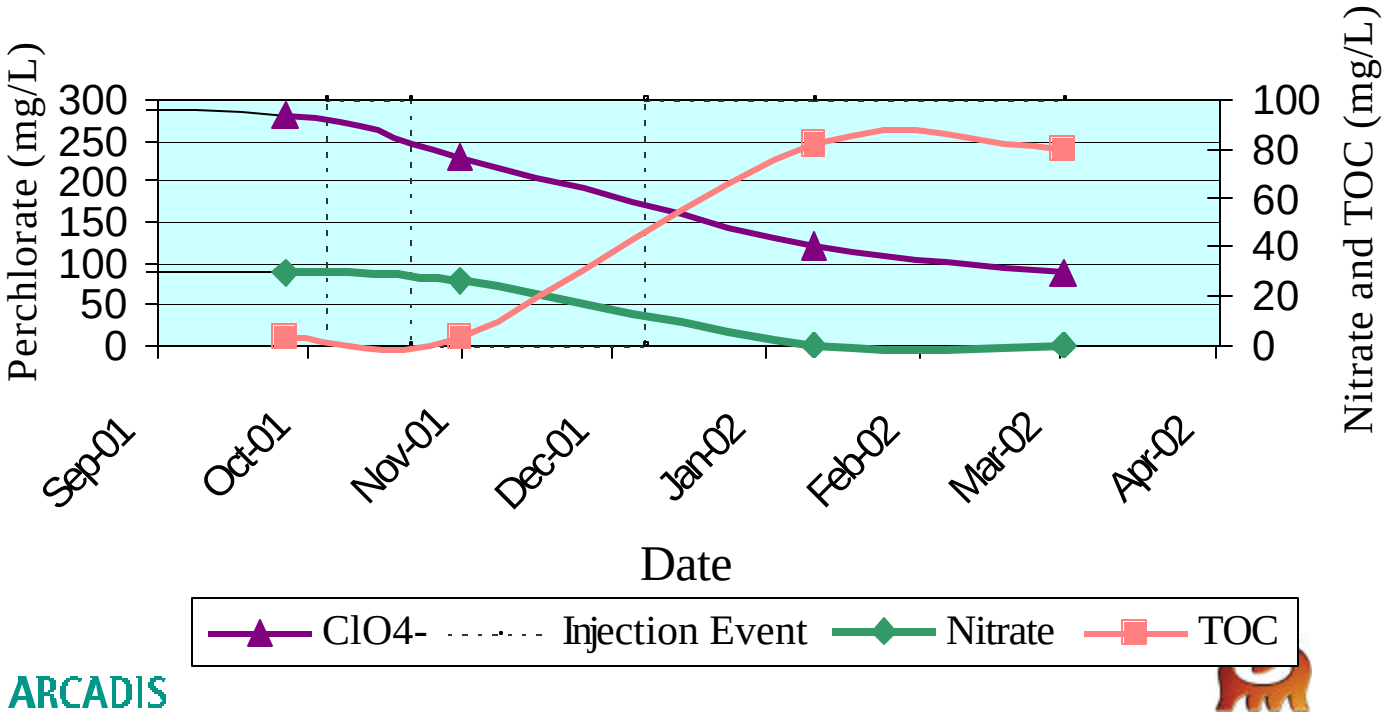


- Injection Well
- Monitoring Well

Treatment Building

Perchlorate Treatment in Silty Sands

IRZ Pilot Results: Perchlorate MW-27



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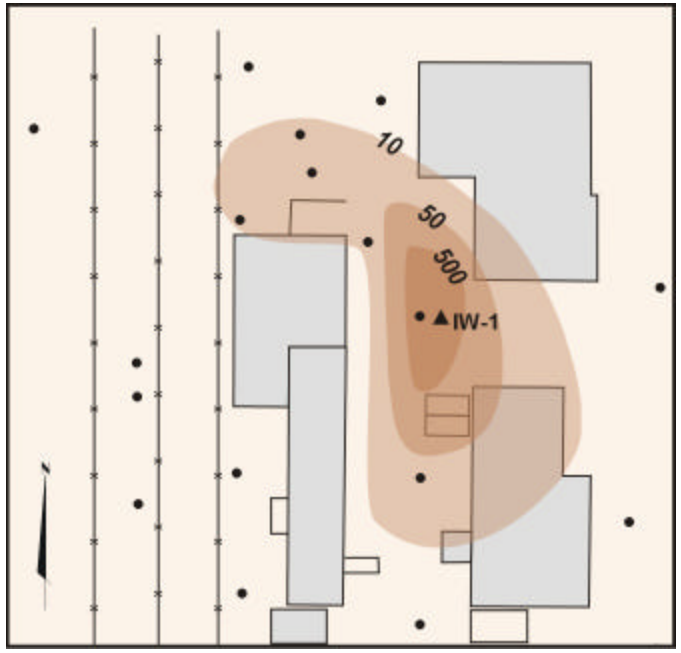
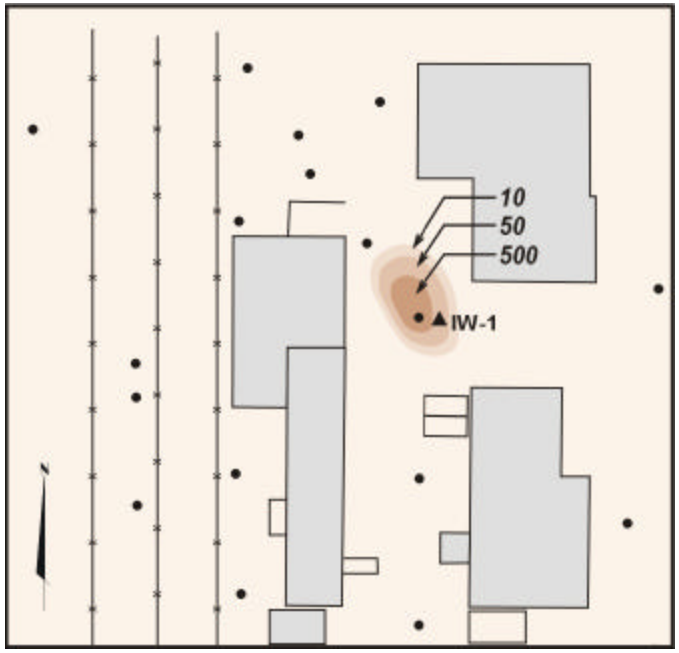
Uranium Treatment in Fractured Shale

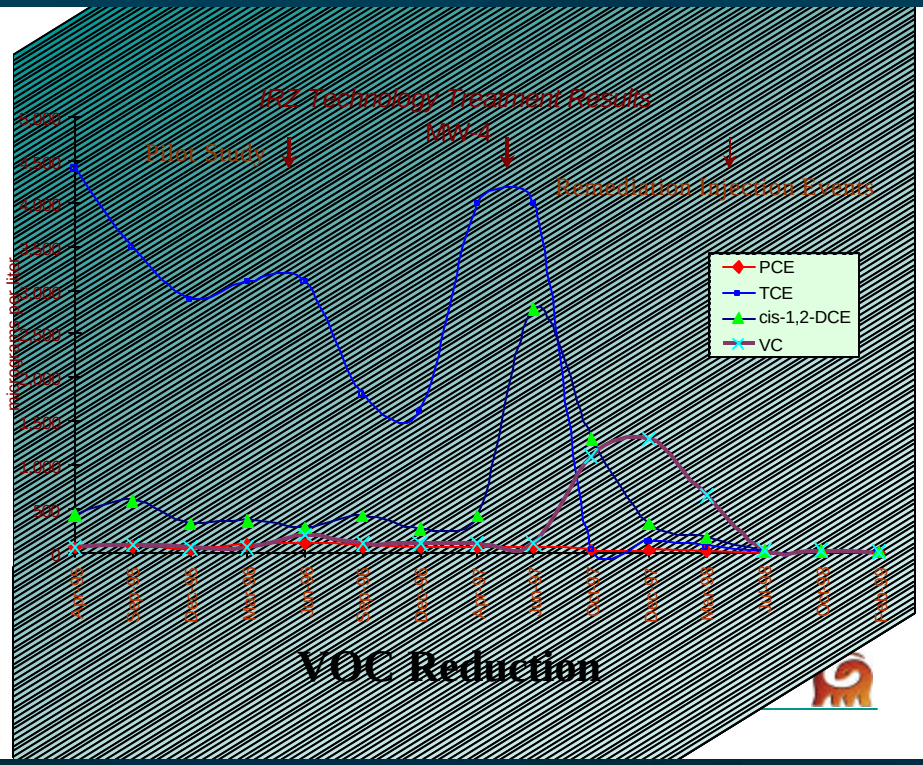


Baseline Dissolved Uranium

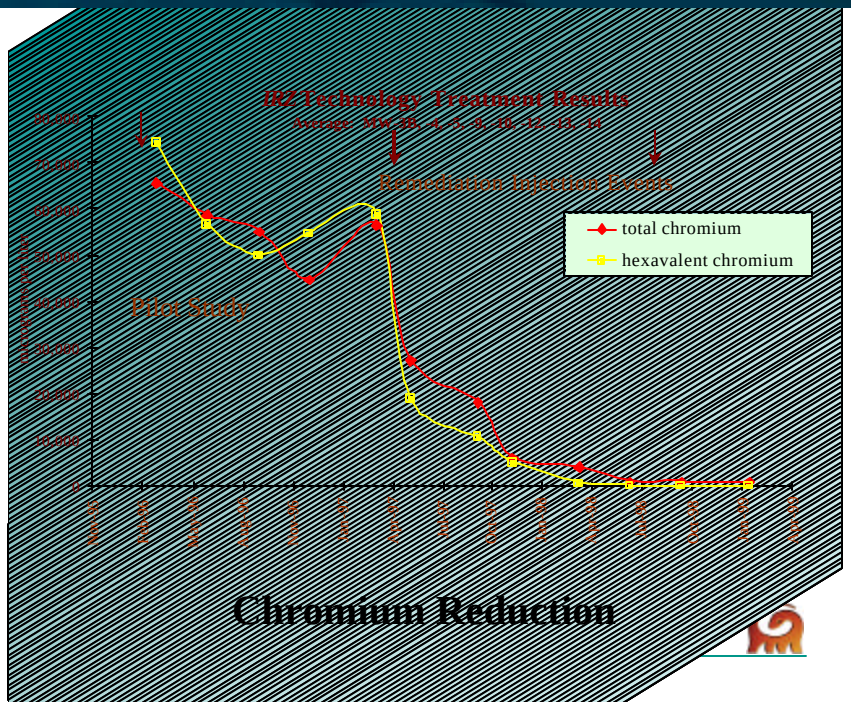


Post Treatment Dissolved Uranium

Molasses and Microbial Injections for Reduction of Chromium and TCE

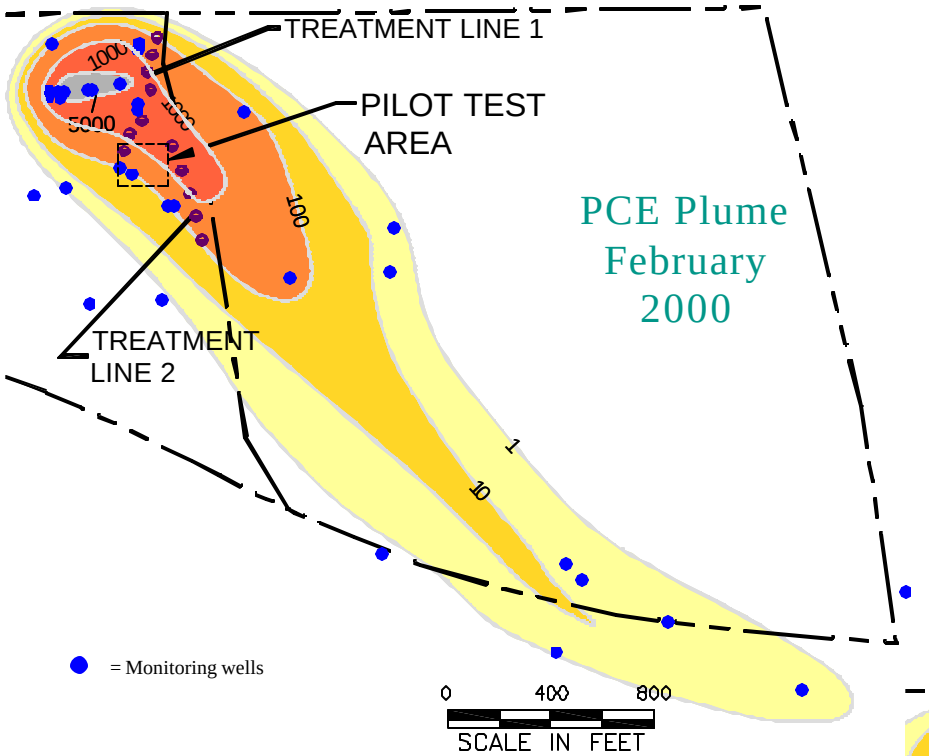


90 injection points installed across si
to 45 feet bls using CPT. Solution
injected every 3 to 6 months.

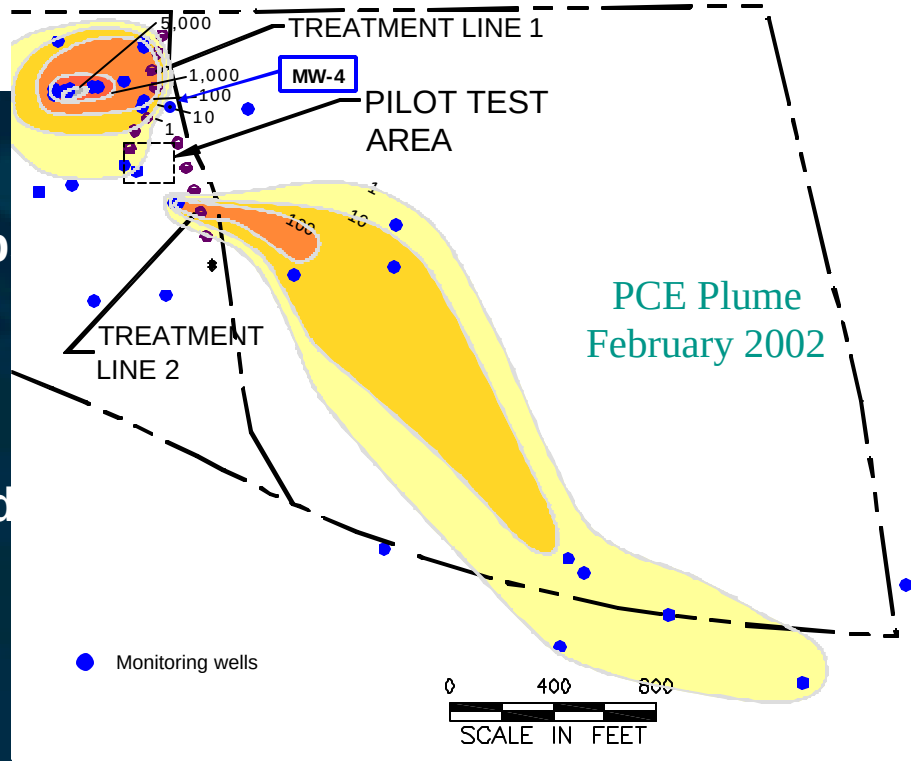


Site closure received 3 years after initiation of remediation

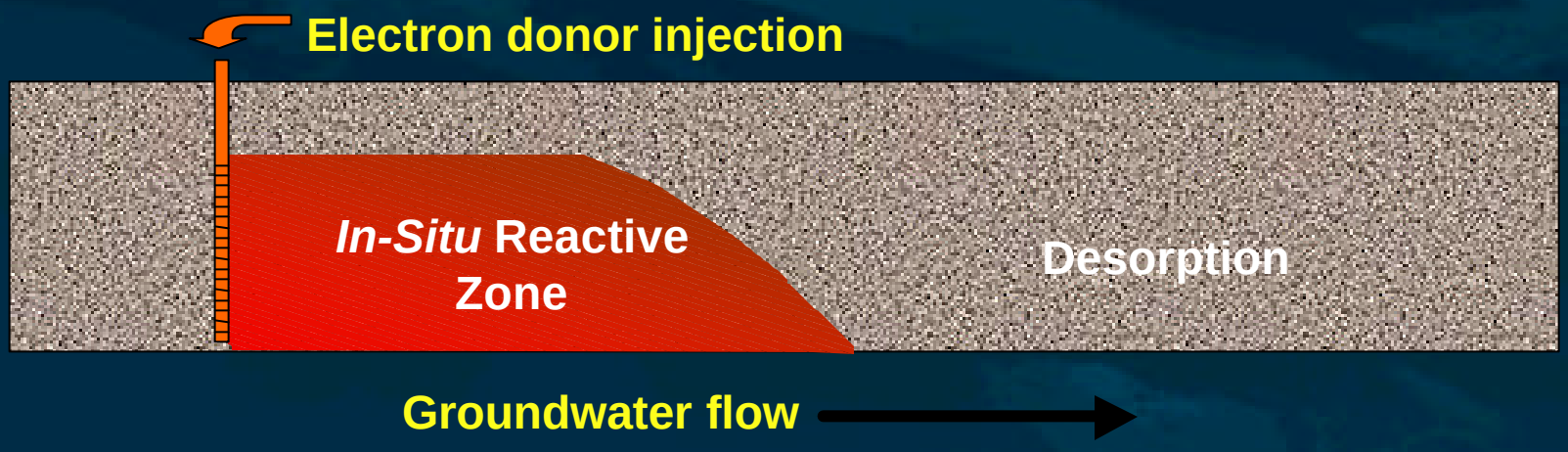
PCE Treatment in Fractured Bedrock Using Molasses:



The full scale mid-plume system consists of 13 wells. The plume map depict the effects of the IRZ on the plume over 20 months of operation. PCE and its daughters were reduced to ND. In the source area 80 ppm PCE was degraded.



Why Use An IRZ?

- Cost Effective Remediation
- Achieve Remedial Goals

Questions?????